



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C23C 14/34		A1	(11) International Publication Number: WO 92/01081 (43) International Publication Date: 23 January 1992 (23.01.92)
<p>(21) International Application Number: PCT/US91/04738</p> <p>(22) International Filing Date: 3 July 1991 (03.07.91)</p> <p>(30) Priority data: 549,392 6 July 1990 (06.07.90) US 671,360 19 March 1991 (19.03.91) US</p> <p>(71) Applicant (for all designated States except US): THE BOC GROUP, INC. [US/US]; 100 Mountain Avenue, Murray Hill, New Providence, NJ 07974 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BELKIND, Abraham, I. [US/US]; 184 Martins Way, North Plainfield, NJ 07060 (US). DOW, Daniel, B. [US/US]; Route 1, Box 490-2, Star, ID 83669 (US). FELTS, John, T. [US/US]; 2624 Calhoun Street, Alameda, CA 94501 (US). LAIRD, Ronald, E. [US/US]; 237 Panorama Drive, Benicia, CA 94510 (US). SCHULZ, Steven, C. [US/US]; 107 Panorama Drive, Benicia, CA 94510 (US). KIRS, Milan, R. [US/US]; 3291 Gloria Terrace, Lafayette, CA 94549 (US).</p>		<p>(74) Agents: PARSONS, Gerald, P. et al.; Majestic, Parsons, Siebert & Hsue, Four Embarcadero Center, Suite 1450, San Francisco, CA 94111 (US).</p> <p>(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN + (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.</p> <p>Published With international search report.</p>	
<p>(54) Title: METHOD AND APPARATUS FOR CO-SPUTTERING AND CROSS-SPUTTERING HOMOGENEOUS FILMS</p>			
<p>(57) Abstract</p> <p>A method and apparatus for depositing thin homogeneous films by dual target reactive sputtering utilizes dual rotating cylindrical magnetrons driven by an electrical potential and which have different sputtering materials. The result is a technique and apparatus of forming a uniform film on large dynamic or static substrates with high deposition rates. A co-sputtering aspect utilizes the orientation of magnetic structures within one or both of the dual targets to promote target cross-contamination between them. A cross-sputtering aspect utilizes one or more rotating cylindrical targets of the same material onto which a different material is coated by sputtering from yet another target, a combination of the two materials being sputtered onto a substrate from the cylindrical target.</p>			

+ DESIGNATIONS OF "SU"

It is under examination in which parts of the former Soviet Union the designation of the Soviet Union has effect.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

METHOD AND APPARATUS FOR CO-SPUTTERING AND
CROSS-SPUTTERING HOMOGENEOUS FILMS

5

10

BACKGROUND OF THE INVENTION

This invention relates generally to sputtering
15 and more particularly to an apparatus and method for
depositing on substrates homogeneous films of two or
more different materials.

Sputtering is the physical ejection of
material from a target as a result of ion bombardment of
20 the target. The ions are usually created by collisions
between gas atoms and electrons in a glow discharge.
The ions are accelerated into the target cathode by an
electric field. A substrate is placed in a suitable
location so that it intercepts a portion of the ejected
25 target atoms. Thus, a coating is deposited on the
surface of the substrate. Sputter deposition of thin
films may be carried out in a variety of systems that
differ in sputtering configuration, geometry, vacuum
system, target type and size, substrate position,
30 temperature, and so forth. Ion beam, diode, and
magnetron systems are examples of sputtering techniques.

With magnetron systems, high sputtering rates can be achieved and high quality coatings can be produced. In a magnetron cathode, a magnetic field is used to confine the glow discharge plasma and to increase the path length of the electrons moving under the influence of the electric field. This results in an increase in the gas-atom electron collision probability. This in turn leads to a much higher sputtering rate than obtained without the use of magnetic confinement. Further, such a sputtering process can be accomplished at a much lower gas pressure.

In planar magnetron systems, the glow discharge plasma is confined by a magnetic structure to an annular region which is parallel to the surface of the flat target plate. In operation, the magnetic confinement of the plasma results in a high rate of erosion in an annular region on the surface of the target. With planar magnetrons, a substrate can be rapidly covered with a metallic coating by using a direct current ("DC") potential to sputter a target plate of the desired metal in a chamber containing an inert gas. However, severe arcing problems are encountered when planar magnetrons are used in reactive sputtering to form certain metal-oxide and other high dielectric coatings. The arcing is due to the formation of a thick dielectric layer on the target surface.

With the advent of rotating cylindrical magnetrons, deposition of heretofore cumbersome dielectric films, such as silicon dioxide, is accomplished without arcing. Generally, in a rotating cylindrical magnetron, a cathode target assembly in the form of an elongated, cylindrical tube carries a layer of material applied to its outer surface that is to be sputtered. The target tube is rotated about its longitudinal axis. A magnetic structure is arranged inside the tube, but does not rotate with it.

It is believed that cylindrical magnetrons can reactively sputter dielectric materials because when the target surface is rotated through the stationary plasma, the top layer of material covering substantially its entire surface is sputtered as that surface is rotated through the magnetic field. Any dielectric that is deposited on a portion of the target surface as it rotates outside the region of the magnetic field is removed by sputtering when it again passes through the field. Layers of dielectric do not form, thereby reducing arcing. This phenomenon may be referred to as a "self-cleaning" characteristic of the rotating cylindrical magnetron. A description of the method employing a rotating cylindrical magnetron for coating substrates with dielectric materials such as silicon dioxide and silicon nitride is found in co-pending application Serial No. 07/433,690, filing date November 8, 1989, by inventors Wolfe et al., of common assignee, incorporated herein by reference.

It is possible with reactive sputtering to prepare a wide range of films having different applications. In addition, new thin films with novel optical, mechanical and chemical properties have been found by combining different sputtered materials such as oxides and nitrides. For example, films containing mixtures of ZrO_2 and Al_2O_3 were produced by sputtering composite targets of zirconium and aluminum and reacting the metal vapor with oxygen. Gilmore, C. M. and Quinn, C., "Stabilization of Tetragonal ZrO_2 with Al_2O_3 in Reactive Magnetron Sputtered Thin Films", J. Vac. Sci. Technol., A5(4), 1987, 2085-2087. See also Misiano, C. and Simonetti, E., "Co-Sputtered Optical Films", Vacuum, 27(4), 1977, 403-406. Some of the mixed oxides have been used in large area optical coatings. See Gillery, "Sputtered Films of Metal Alloy Oxides and Method of Preparation Thereof", U.S. Patent No. 4,610,771.

However, deposition of these mixed oxides was accomplished with single metal alloy targets; and fabrication of alloy targets is limited by the solubility of components, and therefore, by the number of element combinations available. For instance, zinc and tin, two very useful sputtering materials, are non-alloyable. The degree to which different metals can mix poses further restrictions to the use of alloys.

As an alternative to alloy targets, a tailored target made from many alternate metal strips has been introduced to solve the alloy target compatibility problem. See Nomura, K. et al., "Electrical Properties of Al_2O_3 - Ta_2O_5 Composite Dielectric Thin Films Prepared by RF-Reactive Sputtering", J. Electrochem. Soc., 134(4), 1987, 922-925. In some instances, using a tailored or an alloy target is complicated by differences in sputtering conditions and rates of the components. This causes long-term changes in the composition of the target surface and, ultimately, in the film composition. DeNatale, J. F. and Harker, A. B., "Mixed-Cation Optical Thin Films from Tailored Composition Target", Mat. Res. Soc. Symp. Proc., 77, 1987, 181-185.

The problems associated with composite targets are absent when separate cathodes, having targets of different metals, are employed in co-sputtering. Misiano, C. and Simonetti, E., "Co-Sputtered Optical Films", Vacuum, 27(4), 1977, 403-406. With co-sputtering, the composition of the mixed compounds formed is unlimited. But while co-sputtering deposition has been described in the literature, the main theme has focused on two areas: the search for new materials with novel properties and the search for methods of deposition of non-graded (that is, homogeneous) films.

A film co-sputtered from dual magnetron cathodes onto a moving substrate is graded in that the

multi-components therein are not distributed uniformly. A graded film is characterized by having a graded (non-uniform) refractive index. Hanak, J. J., "Co-Sputtering -- Its Limitations and Possibilities", Le vide, No. 175, 5 1975, 11-18. A graded composition is useful for creating very thin interfaces, but optically a graded refractive index is acceptable only for making thick Rugate filters; it is not useful in the manufacture of low-emissivity, solar control, or wide-band, 10 antireflection optical films.

It is a primary object of the present invention to provide an apparatus and method for forming homogeneous films of two or more materials.

It is another object of the present invention 15 to provide a magnetron reactive sputtering apparatus and technique for depositing homogeneous films on large, dynamic substrates.

SUMMARY OF THE INVENTION

These and additional objects are accomplished 20 by the present invention wherein, generally and briefly, cross-contamination by sputtering between two or more targets of different materials is intentionally induced in a magnetron system wherein one of the targets is a rotating cylindrical type that is used in sputtering for 25 depositing homogeneous films. The present invention is applicable to techniques of sputtering with targets connected to either a DC or radio-frequency ("RF") power supply, and to either reactive or non-reactive sputtering methods.

According to a first specific aspect of the 30 present invention, co-sputtering is accomplished by each of two rotating cylindrical targets directing a portion of their sputtered material onto the other target so that each sputters a combination of the two materials 35 onto to form the substrate film. The concept of using

a rotating cylindrical magnetron in reactive sputtering to deposit films of a high dielectric constant, such as silicon dioxide, is generally known. What is surprising is that deposition of homogeneous films comprising 5 different materials can be accomplished by employing dual cylindrical magnetrons in reactive co-sputtering wherein the magnetic structures in each cathode are aligned to cause target cross-contamination. The apparent reason why cross-contamination produces 10 homogeneous films is that by inducing target cross-contamination it is possible to achieve a steady state wherein the combination of materials sputtered from each target are similar. This leads to a uniform deposition of materials onto the substrate. The inventive method 15 and apparatus produces homogeneous films on non-moving as well as dynamic (moving) substrates.

According to a second specific aspect of the present invention, cross-sputtering is accomplished by utilizing one magnetron to sputter its target material onto one or more different material targets of another magnetron without directly forming the film on the substrate. In one embodiment, one magnetron having a target of one material is oriented to cross-contaminate another magnetron having at least one rotating 25 cylindrical target of another material, whereas the magnetic structures in the second magnetron are normal to the substrate. The first magnetron deposits a film onto the target(s) of the second magnetron and avoids directly depositing its material onto the substrate. 30 The material of both magnetrons is then sputtered off the target(s) of the second magnetron and onto the substrate to form a homogeneous film from both of the different target materials.

Such cross-sputtering permits the second 35 magnetron to be optimized for sputtering onto the substrate without the necessity of compromising that

function in order to also sputter onto a target of another magnetron, as is done with the co-sputtering aspect of the present invention summarized above. This can be an advantage in some circumstances.

5 Additional objects, advantages and features of the present invention will become apparent from the following detailed exemplary description, which description should be taken in conjunction with the accompanying drawings.

10

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of a dual rotating cylindrical magnetron sputtering system for depositing homogeneous films according to the present invention;

15

Figure 2 is a cross-sectional view of dual cathode assemblies of a first co-sputtering magnetron embodiment wherein their magnetic assemblies are tilted toward each other;

20

Figure 3 is a schematic representation of film deposited on a dynamic substrate using dual cathode wherein the magnetic structures are not tilted;

Figure 4 is a graph comparing the refractive index of films as a function of the films' position vis-a-vis dual cathode assemblies;

25

Figure 5 is a graph of the atomic ratio (%) of tin to tin and zinc of films as a function of the films' position vis-a-vis dual cathode assemblies;

30

Figure 6 is an Auger profile of an $\text{Al}_2\text{O}_3/\text{SiO}_2$ film co-sputtered from a dual rotating cylindrical magnetron wherein the magnetic structures are tilted at 15°;

Figure 7 is an Auger profile of an $\text{Al}_2\text{O}_3/\text{SiO}_2$ film co-sputtered wherein the magnetic structures are at 25°;

Figure 8 is a cross-sectional view of dual cathode assemblies of a second co-sputtering magnetron embodiment that includes a control system;

5 Figures 9A and 9B are curves that illustrate the operation of the magnetron of Figure 8;

Figure 10 is a flow diagram that sets forth a process of adjusting the control system of the magnetron of Figure 8;

10 Figure 11 is a graph of the atomic ratio (%) of zirconium to zirconium and titanium in a film as a function of position across a deposition zone for different directions of rotation of dual targets;

15 Figure 12 is a graph of the atomic ratio (%) of tin to tin and zinc in a film as a function of position across a deposition zone for two different speeds of rotation of dual targets;

Figure 13 is a cross-sectional view of a dual rotating cylindrical target magnetron in a first cross-sputtering embodiment;

20 Figure 14 is an alternate cross-sputtering magnetron sputtering embodiment, shown in cross-section; and

Figure 15 shows a modification of the magnetron of Figure 14.

25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention will be explained with respect to implementing the dual rotating cylindrical magnetrons that are generally illustrated in Figure 1. A plasma is formed in an enclosed reaction chamber 10, in which a vacuum is maintained, where a substrate, such as substrate 12, is placed for depositing a thin film of material upon it. The substrate 12 can be any vacuum compatible material, such as metal, glass, and some plastics. The substrate can be stationary or moving. The film can also be deposited

over other films or coatings that have previously been formed on a substrate surface.

Each of the cathode assemblies 14 and 114 comprises generally an elongated cylindrical tube 16 mounted in the reaction chamber 10. An elongated magnet assembly 18 is carried within a lower portion of the tube 16, extends substantially its entire length, and is restrained against rotation with it. The cathode assemblies are substantially parallel to each other. In order to operate at high electrical power levels, desirable in order to have a high film deposition rate, the tube 16 is preferably cooled by passing water or another heat transfer fluid through it.

The tube 16 is formed of a suitable non-magnetic material such as, for example, brass or stainless steel, and is of a diameter, wall thickness and length required for a particular operation to be performed. Applied to the outer surface of tube 16 of cathode assembly 14 is a layer of a selected target material 20 to be deposited onto the substrate 12 being coated. Similarly, applied to the outer surface of tube 16 of cathode assembly 114 is a layer of selected material 120. The selected materials 20 and 120 are different in the co-sputtering process.

The tube 16 in each cathode assembly is supported in a manner to be rotated about its longitudinal axis by a target drive system 22. The orientation of the longitudinal axis depends upon the shape and position of the substrate that is being coated. In the example being described herein, the substrate 12 is held horizontally and is flat, and the longitudinal axis of the tube 16 is also horizontal, thus being parallel with the substrate surface to be coated.

In a preferred arrangement, somewhat different from the schematic representation of Figure 1, the tube

16 is rotatably held at each end in a horizontal position. A support structure at one end also allows cooling fluid to be introduced into the tube 16 and withdrawn from it, and contains a mechanism for driving 5 the tube 16 from a motor source outside of the vacuum chamber 10. Rotating seals are included in this support structure for isolating the cooling fluid from the vacuum chamber. A support structure at an opposite end includes an electrical brush assembly for connecting the 10 tube to a negative voltage.

The magnetic assembly 18 in each cathode assembly comprises an array of magnetic poles arranged in straight parallel rows along the length of the tube 16. Each row has three alternating magnetic poles 24, 15 26 and 28. In one configuration, the poles 24, 26 and 28 are arranged to have respective north, south and north polarities. An opposite configuration of 20 respective south, north and south polarities may also be used. In either case, the magnetic poles 24, 26 and 28 are positioned in relation to the tube 16 so that their lines of force run from one pole, through the tube 16, and back through the tube in a curved path to an adjacent pole having an opposite polarity. This 25 arrangement generates what is called a magnetic tunnel, which not only allows the sputtering rate to be increased, but also causes the target materials 20 and 120 to be removed faster inside the tunnel, especially in the middle of this magnetic pattern.

As shown in Figure 1, the magnetic structure 30 in each tube is rotated on its axis towards the center of the cathode assemblies. Figure 2 shows a cross-section view of the dual cathode assemblies. In cathode assemblies 14 and 114, the angles at which the magnetic structures are rotated are designated as θ_1 and θ_2 , 35 respectively. It should be noted that θ_1 and θ_2 need not be identical, and indeed, as described herein, depending

on the sputtered materials, in some preferred embodiments the angles are different. Each of these angles can range from zero degrees to ninety degrees, depending upon various other parameters, non-zero angles often lying in a range of from 25-50 degrees. The target surfaces 14 and 114 each usually include a single sputterable element different from the other, the following elements typically employed, for example, in glass coating: aluminum, indium, nickel, silicon, tantalum, tin, titanium, zinc, boron, tungsten, niobium, hafnium, magnesium, silver, ruthenium, vanadium, chromium, molybdenum, bismuth and zirconium. In addition to one of these or some other element, the target surfaces 14 and 114 generally contain minor amounts of other elements to provide structural integrity, promote sputtering, and for other similar purposes.

As is apparent from Figures 1 and 2, increasing θ_1 , from zero, where the magnetic structure is normal to the substrate, increases the amount of target cross-contamination onto cathode assembly 114. Similarly increasing θ_2 promotes cross-contamination of cathode assembly 14. Though not to be viewed as a limitation to the invention, it is believed that by adjusting the angles and thus inducing target cross-contamination, it is possible to achieve a steady state wherein the materials sputtered from each tube are similar. For instance, in a situation involving dual cathodes A and B coated with materials x and y, respectively, by adjusting θ_1 and θ_2 , it is possible to establish an equilibrium wherein the flux of x and y toward the region of the substrate 12 from both targets is substantially the same.

The amazing result of promoting cross-contamination is an improvement in the composition homogeneity of the films deposited on a moving

substrate. This is to be contrasted with co-sputtering without cross-contamination. As illustrated in Figure 3, normally a film deposited on a dynamic substrate using dual cathode co-sputtering (where θ_1 and θ_2 are both zero) exhibits a graded structure depicted as the simplified 3-layer model. As the substrate 150 enters the deposition chamber, the obliquely sputtered flux 152 from the first target 154 is deposited first to form layer 166. Thereafter, the combination of fluxes 156 and 166 from the first and second targets 154 and 164, respectively, form the second and principal layer 160 of interest, which is the co-sputtered film. The last flux 162 is from the second target and results in the third layer 168. The first layer 166 has a graded composition starting from the almost pure first target material to the composition of the second layer 160. The composition of the second layer 160 can be changed by varying the cathode potentials. Heretofore, the composition of the second layer was non-homogeneous. However, sufficient cross-contamination in the present invention in co-sputtering is believed to lead to a decrease in thicknesses of the first and third layers, and an increase in the thickness of the second layer, as well as the homogeneity of this layer.

That cross-contamination actually enhances production of homogeneous films is rather unexpected because target cross-contamination has been considered a problem associated with magnetron co-sputtering. Hanak, J. J., "Co-Sputtering -- Its Limitations and Possibilities", Le vide, No. 175, 1975, 11-18, and Hanak, J. J. and Klopfenstein, R. W., "Model of Target Cross-Contamination during Co-Sputtering", RCA Review, 37, 1976, 220-233. For example, when using dual rotating cylindrical magnetrons for depositing metal films, the magnetic structures in each of the magnetrons can be oriented relative to one another such that the

magnets thereof are at an acute angle and direct the sputtered material downwardly and inwardly to focus it upon the substrates that are located therebeneath. Due to this magnetic arrangement, the material sputtered from the two targets is focused onto a relative small area of the substrate, thereby improving the deposition rate. McKelvey, "Magnetron Cathode Sputtering Apparatus", U.S. Patent 4,466,877.

As stated above, it may not be necessary to maintain the rotated magnetic structures at the same angle, and indeed, depending on the material to be co-sputtered, the optimum conditions may be such that the angles are not the same. This phenomenon is evident in co-sputtering SnO_2 and ZnO where symmetric co-sputtering, that is, where the angles of the magnetic structures in the dual cylindrical magnetrons are the same, did not yield homogeneous films. It is believed that the non-homogeneity distribution is attributable to the different re-sputtering rates of Sn and Zn. As will be described below, surprisingly homogeneous films comprising SnO_2 and ZnO were produced in asymmetrical sputtering, that is, where the angles of the magnetic structures in the dual cylindrical magnetrons are different.

In another embodiment of the invention, θ_1 and θ_2 are set at 0° and 90° , respectively. In this embodiment, target 14 is cross-contaminated by material sputtered from target 114; and the substrate, in turn, is deposited with materials sputtered from target 14.

The arrangement of the magnetic assembly 18 in Figure 2 is a "W" configuration of three elongated magnets 24, 26 and 28. An alternative is a "U" configuration wherein a single magnet is positioned in the middle and a "U" shaped piece of magnetic material is positioned to form poles on either side of the magnet and of opposite polarity. In either case, it is usually

desirable to position the pole faces as close to an inner surface of the tube 16 as possible. The magnetic assembly 18 is preferably supported within the tube 16 from a stationary axial rod or cooling fluid tube.

5 A cathode potential, V , sufficient to cause sputtering to occur is supplied to the tubular targets 16 in each cathode assembly from DC power sources 30 and 230 through a power lines 32 and 232 having sliding contacts 34 and 234 with the tubes 16 by a conventional 10 electrical brush. The enclosure of the reaction chamber 10 is conductive and electrically grounded. It can serve as an anode in the sputtering process. A separate 15 anode may be optionally employed and maintained at a small positive voltage. Such an anode is positioned for example above the target tubes and is preferably water cooled in order that high power levels may be employed.

In order to obtain the low pressure necessary for the coating operation to be performed, the reaction chamber 10 is provided with an outlet tube 36 20 communicating with a vacuum pump 38. A gas supply system provides the chamber 10 with the gases necessary for the coating operation. A first gas supply tube 40 extends into the coating chamber 10 and from a source 42 of an inert gas. The inert gas is preferably argon for 25 the specific methods being described. Nozzles 44 connected to inlet tube 40 distribute the inert gas in a region above the rotating cathodes. It is the inert gas that breaks down into electrically charged ions under the influence of an electric field established 30 between the target surfaces 20 and the grounded chamber enclosure or separate floating anode. The positive ions are attracted to and bombard the target surfaces 20 and 120, under the influence of the electric field. For 35 each target, this bombardment occurs primarily in two parallel strips, one between each of the opposing magnetic poles, along the length of the cylinder at its

bottom, opposite the magnet assembly 18. Thus, as each tube is rotated, its target surface is rotated through these two parallel strips. Some of the molecules sputtered from one target will be deposited onto the 5 other target. As described above, the amount of cross-contamination can be controlled by adjusting θ_1 and θ_2 .

A second gas supply tube 46 extends through the coating chamber 10 from a reactive gas source 48. Nozzles 50 connected to inlet tube 46 distribute the 10 reactant gas close to and across the width of the substrate 12 being coated. Molecules of the reactive gas combine with molecules sputtered from the target surfaces, as a result of ion bombardment, to form the desired molecules that are deposited on the top surface 15 of the substrate 12.

Many variations in the gas supply system shown are practical as well. The inert and reactive gases from the sources 42 and 48 can be combined and delivered into the chamber 10 through a common tube and set of 20 nozzles. When this is done, the delivery tube is preferably positioned along a side of the rotating target tubes 16 and parallel with its longitudinal axis. Two such tubes can be used, one on each side of the target tubes 16 and parallel with its longitudinal axis, 25 each delivering the same combination of inert and reactive gases. Also, more than one reactive gas can be simultaneously supplied, depending upon the film being deposited.

Experimental Results

30 Experiments utilizing the inventive method were conducted in an ILS-1600 Airco Coating Technology System having rotatable 3" diameter dual cathodes (C-MAG™ 750) with independent power control. The targets were conditioned using an inert gas, then the process 35 gas was added until the desired partial pressure was

reached. The process was operated at that point until stabilized. The substrates were then introduced to the coat zone and the film was applied. The substrates used were 4"x4" soda lime glass.

5 When using dual magnetrons, the direction in which each cathode is rotating can vary. For example, both targets can be rotating in the same direction, either clockwise or counterclockwise, or the targets can be rotating in different directions. Practice of the
10 invention is not limited by the direction the targets rotate. However, in the experiments described herein, targets were rotated counterclockwise having the substrate moving from left to right. The rotation speed was 8 r.p.m.

15 Reactive Sputtering and Co-Sputtering on a Static Substrate

Reactive sputtering individual films of Al_2O_3 and TiO_2 , and symmetrically reactive co-sputtering of the same were conducted using the above-described dual cathode assemblies wherein θ_1 and θ_2 were fixed at 30°. 20 Al_2O_3 and TiO_2 were sputtered at 3 kW and 6 kW, respectfully. Targets of cathode assemblies 14 and 114 were titanium and aluminum, respectively. When sputtering only TiO_2 , the potential of cathode 114 (Al) was zero and conversely when sputtering only Al_2O_3 , the 25 potential of cathode 14 (Ti) was zero. The substrates were static; that is, not moved once set in place.

30 Table 1 sets for the process data for production of the films. The potentials refer to the potential between the respective cathode assembly tube and the ground. The power refers to the power supplied. The current was measured at the power source. The flow rates of the inert gas and reactive gas were measured in standard cubic centimeters per minute (SCCM). The pressure of the reaction chamber is measured in microns.

TABLE 1

Film	Power*	Potentials*	Pressure	SCCM	SCCM
	(kw)	(v)	(μ)	O ₂	Ar
Al ₂ O ₃	3	328	2.7	15	35
TiO ₂	6	605	2.7	23	28
Al ₂ O ₃ +TiO ₂	3/6	450/642	2.6	16	32

* The first value refers to cathode 14 (Al) and the second refers to cathode 114 (Ti).

Figure 4 is a graph of the refractive index of each film as a function of the film's position vis-a-vis the two cathode assemblies. On the horizontal axis, positions 5.0 and 20.0 designate substrate positions directly below the cathode assemblies 14 (Al) and 114 (Ti), respectively, and 12.5 cm designates the point on the substrate midway in between. As can be seen from the graph, directly under the aluminum target, the refractive index of the Al₂O₃ (curve 310) is 1.65 whereas directly under the titanium target the refractive index of TiO₂ (curve 320) is 2.4-2.5. Far from the targets, the refractive index decreased to only 1.55 and 2.0-2.2 for Al₂O₃ and TiO₂, respectively. In contrast, the refractive indices of the co-sputtered Al₂O₃/TiO₂ film (curve 330) changed only slightly with substrate position along the center line, which indicates that the variation in composition of the Al₂O₃/TiO₂ film was not significant.

Symmetric and asymmetric reactive co-sputtering of SnO₂ and ZnO on a static substrate was conducted. In these co-sputtering experiments, both the angles of the magnetic structures and the power to each target were varied. In these studies, cathode assembly 14 was coated with tin and cathode assembly 114 was coated with zinc. Table 2 sets forth the four different operative conditions studied.

TABLE 2

	Angle θ_1 (Sn)	Angle θ_2 (Zn)	Power (kW)	Potentials* (V)	Pressure (μ)	SCCM	SCCM
	Film					O_2	Ar
5	170	30°	30°	0.4/0.7	368/450	10.0	92.0 0.0
	172	45°	30°	0.4/0.7	384/462	8.5	92.0 0.0
	174	45°	30°	0.6/0.5	410/423	9.0	92.0 0.0
	176	45°	30°	0.6/0.25	429/390	9.0	92.0 0.0

* The first value refers to cathode 14 (Sn)
and the second refers to cathode 114 (Zn).

Figure 5 is a graph of the atomic ratio (%) of tin to tin and zinc on the films as a function of the film's position vis-a-vis the cathodes. In the case of symmetrical sputtering, θ_1 and θ_2 were both fixed at 30°, with power to the tin and zinc targets set at 0.4 kW and 0.7 kW, respectively. As shown on curve 170, the tin concentration in the symmetric co-sputtered films, deposited along the center line, varied for more than 10%. However, by increasing cross-contamination of the zinc target, this variation was reduced significantly. Specifically, as illustrated in curve 172, simply by increasing θ_1 to 45° for the tin-coated cathode, a reduction in the variation of concentration distribution of tin is achieved to 2%. Moreover, increasing the tin concentration in the co-sputtered films by varying the power levels for the tin and zinc targets, namely, to 0.6 kW and 0.5 kW, and 0.6 kW and 0.25 kW, respectively, did not adversely affect the improved tin distribution. The variation in tin concentration remained relatively low, 2% and 1.5%, respectively, while the absolute tin concentration increased, as shown in curves 174 and 176, respectively.

Homogeneous composition distributions obtained in these experiments with static substrates suggest that co-sputtering on dynamic substrates should produce films with homogeneous compositions as well. This assertion was confirmed in the co-sputtering experiments described herein.

Co-Sputtering on a Dynamic Substrate

5 In industrial applications, it is not uncommon for a coating process to be a continuous one where substrates are coated as they move across the target assembly. With the present invention, film homogeneity is maintained even when co-sputtering on dynamic substrates.

Reactive Symmetric Co-Sputtering of Al_2O_3 and SiO_2 at 15° and 25° on a Dynamic Substrate

10 Using the dual cathode magnetron described above, reactive symmetric co-sputtering of Al_2O_3 and SiO_2 was conducted on dynamic substrates. Two magnetic structure angles, 15° and 25°, were chosen. Table 3 sets forth the operating conditions of the co-sputtering.

TABLE 3

Angle	Thickness (Å)	No. of Passes	Power* (kw)	Potential* (v)	Pressure (μ)	SCCM O_2	SCCM Ar
15°	1525	4	5.5/1.0	360/339	1.66	23	35
25°	1320	4	5.5/1.0	364/340	1.70	23	35

* The first value refers to cathode 14 (Al) and the second refers to cathode 114 (Si).

25 During deposition, the substrate was transported back and forth across the plasma, and the number of passes refers to the number of times the substrate crossed the plasma during the sputtering process at a particular time. Composition analysis of each film was made with Auger electron spectroscopy. Figure 6 is an Auger profile of the $\text{Al}_2\text{O}_3/\text{SiO}_2$ film co-sputtered at 15°. The profile shows that the amount of oxygen (curve 180) in successive layers of the film remains relatively constant throughout the co-sputtering process. In contrast, the amount of aluminum (curve 182) varies significantly, with the concentration

following a sinusoidal-like pattern beginning from a relatively high concentration. Similarly, the amount of silicon (curve 184) in the layers of the film varied and also followed a sinusoidal pattern. However, in contrast to aluminum, the silicon pattern began at a relatively low amount. The Auger analysis detected a slight amount of carbon (curve 186) contamination in the film.

The Auger profile indicates that symmetric co-sputtering of Al_2O_3 and SiO_2 at magnetic angles of 15° on a dynamic substrate produces a film with a non-homogeneous composition. Indeed, the profiles of aluminum and silicon confirm that Al_2O_3 and SiO_2 are deposited at different rates depending upon the substrate's position relative to the aluminum and silicon targets. In contrast, the Auger profile as shown in Figure 7 shows that aluminum (curve 190) and silicon (curve 192) are deposited at relatively constant rates when co-sputtering takes place at 25° . Curves 194 and 196 refer to the oxygen and carbon contents of the film, respectively. It is believed that when co-sputtering at 25° , there is sufficient cross-contamination of the targets so that the flux of aluminum and silicon from each target is substantially the same. Thus, the film deposited is homogeneous.

25 Co-Sputtering Process Control

A generalized version of the co-sputtering system of Figures 1 and 2 is given in Figure 8, wherein several of the parameters of operation of the sputtering apparatus are individually controllable. The rotatable position of the magnets, the power applied to each target and the speed of rotation of each target are cooperatively adjustable in order to obtain a film deposited on a substrate that contains a desired homogeneous mixture of compositions formed from each of the targets.

Referring to Figure 8, adjacent rotating cylindrical magnetron target assemblies 201 and 203 include respective cylindrical targets 205 and 207 which rotate about their respective axes 209 and 211. 5 Provided at the outside of the targets 205 and 207 are different materials, denoted as M1 and M2, respectively, to be sputtered into a common substrate film. Fixed within the rotating cylindrical targets 205 and 207 are respective coolant tubes 213 and 215 to which magnetic 10 assemblies 217 and 219 are attached. The magnet assembly 217 includes pole faces 221, 223 and 225, and the magnetic assembly 219 contains pole faces 227, 229 and 231.

The magnetic assemblies 217 and 219 are 15 rotatably positionable in order that respective axes 233 and 235 are set at desired angles θ_1 and θ_2 with respective vertical references 237 and 239. The magnets confine the plasma of the outside of the respective targets to the define erosion zones inbetween adjacent 20 magnetic poles where sputtering of target material is the greatest. Such erosion zones or tracks 241 and 243 are indicated for the target assembly 201 and similar erosion zones 245 and 247 are indicated for the target assembly 203. These sputtering tracks or erosion zones 25 are held stationary while their cylindrical targets are rotated through them to deposit film on a substrate. The circumferential positions of the erosion zones are repositionable by rotation of their respective magnetic assemblies with respect to their supporting coolant 30 tubes. The position of the erosion zones then determines the direction at which the particles are sputtered from their respective targets, a desired balance being obtained between material being sputtered downward directly onto a moving substrate 249 and the 35 amount sputtered across to the adjacent target surface.

Each of the cylindrical targets 205 and 207 is rotated by a motor source indicated schematically by drives 251 and 253, respectively. The greatest flexibility in adjustment is provided if each of the 5 targets is driven by a separately controllable motor source, but satisfactory results are also obtained when driven by a single variable motor source coupled to both of the cylindrical target assemblies by an appropriate system of gears. The desired direction of rotation, as 10 indicated in Figure 8, is for the right-hand target to be rotated in a clockwise direction and the left-hand target to be rotated in a counterclockwise direction, for reasons stated hereinafter.

Similarly, each of the magnetic assemblies 217 15 and 219 is made adjustable in rotational position by motor sources indicated schematically at 255 and 257. It is desirable that the angle of each of the stationary magnetic assemblies 217 and 219 be independently adjustable for the contemplated deposition processes. 20 Each of the targets 205 and 207 is also coupled to separately controllable power sources 259 and 261. The adjustable speed of rotation, power and magnetic rotatable position are determined and set by an appropriate electronic control system 263.

25 A detailed mechanical structure of a preferred rotating target assembly for use with large substrates, such as architectural glass, is given in copending application Serial No. 609,815, filed November 6, 1990, by Alex Boozenny et al. Similarly, a preferred system 30 for rotatably positioning the magnetic assemblies 217 and 219 is given in copending application Serial No. 647,372, filed January 29, 1991, by Barney et al, wherein the magnet rotation means 255 and 257 are electrical stepper motors. Further, it is often desired 35 to employ a cylindrical shield partially surrounding each of the targets, such as disclosed in copending

patent application Serial No. 647,391, filed January 29, 1991, by Kirs et al. Each of these three applications is of common ownership with the present application, and is expressly incorporated herein by this reference.

5 Each of the target assemblies 201 and 203 and associated elements are, of course, contained within a vacuum chamber of the type described schematically with respect to Figure 1. Although the apparatus of Figure 8 can be used to deposit films on stationary substrates, 10 that being described herein is specifically adapted for depositing homogeneous films on a substrate 249 that is moving under the target assemblies by supporting rollers 265 or another convenient mechanism. Conduits 267 and 269 are also provided within the vacuum chamber in order 15 to introduce an inert gas (such as argon) and/or a reactive gas (such as oxygen) in order to support the sputtering operation and react with the material sputtered off the targets. Inert and reactive gases can be introduced through the same conduits, but it is 20 generally preferred to introduce the reactive gas near the substrate and the inert gas near the target assemblies.

The high degree of adjustability is provided in the system of Figure 8 in order to be able to carefully control the relative compositions and 25 homogeneity of a film being deposited on a substrate. The given magnetron apparatus will have certain fixed parameters, such as dimensions of vacuum chamber, diameter of targets, magnetic pole spacing, distance between target and the substrate, distance between 30 target assemblies, and the like. But within these and similar constraints of a given piece of apparatus, the independent adjustability of magnetic rotatable position, target power and target rotational speed allows the relative proportions of elements derived from 35 each of the two targets to be adjusted in a manner to maintain homogeneity of the film being deposited.

Figures 9A and 9B provide exemplary curves intended to illustrate the effect of the three adjustments of the system of Figure 8. A curve 271 illustrates generally a typical deposition rate from the target assembly 201 by itself, when totally isolated from the other target assembly 203. The rate of deposition, and thus the thickness deposited upon a stationary substrate under it, is highest where the most material is being sputtered from the erosion zones 241 and 243. Similarly, a curve 273 indicates the rate of deposition across a stationary substrate from the target assembly 203 when operating by itself without any influence of the other target assembly 201.

Such separate operation is, of course, only discussed as an aid to understanding the effect of the adjustments provided by the system of Figure 8 since it is not intended that the system be operated in this manner, although it certainly can be. Adjusting the direct current power applied to each of the target assemblies by supplies 259 and 261 will generally cause their respective curves 271 and 273 to rise or fall generally uniformly over the substrate. Rotation of the magnetic assemblies 217 and 219, through the magnetic rotation controls 255 and 257, will cause the respective curves 271 and 273 to be weighted to the one side or the other, depending upon the direction of magnet rotation. The speed of rotation of the targets 251 and 253 has no effect. Nor does the direction of rotation of the cylindrical targets affect their individual film sputtering characteristics.

However, when the different materials M1 and M2 of the targets 205 and 207 are to be combined in a homogeneous composition film on a substrate, rather than being deposited separately, the co-sputtering effect between the targets makes all of the rotational direction, rotational speed, target power and magnet

position affect the composition and homogeneity of the resulting film. Figure 9B shows an example deposition rate characteristic that is desired and achievable by properly making these adjustments. Curves 275 and 277 5 show the relative deposition rate of materials M1 and M2 across the vacuum chamber between extreme positions A and B from materials of the targets 205 and 207, respectively. It is not necessary that the deposition 10 rate of these two materials be the same across the deposition zone, but rather that they have the same relative proportion or ratio within a few percent. The film then deposited on the substrate 249 as it passes between points A and B within the vacuum chamber has substantially the same composition at all levels, in 15 contrast to the situation explained earlier with respect to Figure 3.

The effect of rotatably repositioning the magnet assemblies 217 and 219 in a co-sputtering system is to change the shape of their respective material 20 deposition curves as well as shifting any peaks that exist. For example, if the magnetic assembly 217 of the target assembly 201 is rotated a few degrees counterclockwise, more material of the target 205 is sputtered off of it and onto the target 207, and then 25 resputtered from the target 207. More of the material of the first target 205 is then deposited to the right-hand side of the chamber near the edge B. At the same time, the relative amount deposited near the edge A of the vacuum chamber is reduced.

30 It has also been found that the direction of rotation of the targets 205 and 207 affects the distribution of the deposition rate of their respective materials across the vacuum chamber. The direction of rotation indicated in Figure 8 is generally preferred 35 since it has been found to increase the deposition of

the deficient materials at the tails of the distribution curves while reducing their peaks.

The speed of rotation of each of the targets affects the amount of material of the other target that is allowed to accumulate on its surface and thus the proportions of each material that is sputtered from it. Generally, it has been found preferable to rotate the targets at a higher speed than usual in order to keep relatively thin the amount of material deposited on each target surface from the other.

In the co-sputtering situation, adjustment of the target power 259 and 261, in most cases, mostly controls overall the amount of material that is sputtered off of the respective targets but also affects slightly the shape of the deposition rate curves. The relative power level adjustment provides the most direct control of the relative proportions of the materials sputtered from the two targets.

Figure 10 is a process flow chart which illustrates the steps of adjusting a magnetron of the type of Figure 8 prior to production film depositions being made. A first step 279 is, of course, to know what is desired in the film. For example, a mixed tin oxide and zinc oxide film is deposited on the substrate 249 by one target 205 containing substantially pure tin and the other target 207 containing substantially pure zinc on their outside surfaces. Oxygen is then introduced into the chamber through conduits 267 and 269 as a reactive gas in order to form the oxides from each of these materials. A certain atomic ratio of the tin oxide to zinc oxide material in the film will be desired and specified.

A next step 281 is to adjust the values of the three parameters for each of the target assemblies, namely power, magnet position and rotation speed. In making this first "guess" of these parameters, any

difference in the sputtering rates of the tin and zinc material from their respective targets is taken into account. Adjustment of the power supplied to each target principally compensates for this difference, but 5 the magnet angle also does so.

Once the parameters are set, test films are deposited in a step 283. It is preferable that individual substrate pieces be positioned periodically across the deposition zone between edges A and B of the 10 vacuum chamber. After deposition, the film is analyzed for homogeneity and composition by standard techniques. If the first setting of parameters results in the desired homogeneous film at all positions in the chamber, as determined in a step 285, then the system is 15 adjusted for a production run. However, if the desired homogeneity is not present, the position and extent of the non-homogeneity is analyzed as part of a step 289 to readjust one or more of the three parameters for each of the target assemblies, and then test that setting again 20 in the step 283. This is done as many times as is necessary in order to obtain the desired results.

Rotation Direction and Speed Experimental Results

The curves of Figures 11 and 12 each show the effects on the relative concentrations of two elements 25 in a film deposited in a specific experimental implementation of the systems described with respect to Figures 2 and 8, where only one of the parameters discussed above was changed at a time. These experiments were conducted in an ILS-1600 Airco Coating 30 Technology coater having two rotatable targets that are each of 3 inches in diameter. A number of small glass substrates were statically positioned in a path across the deposition zone oriented perpendicularly to the axes of rotation of the targets. The resulting films 35 deposited on the substrate pieces were analyzed to

provide their film characteristics shown in Figures 11 and 12. The films were formed by reactive sputtering of the target materials in oxygen. Figure 11 illustrates the effect on a film of two different directions of target rotation, while the effect of two different speeds of rotation are shown in Figure 12.

Referring to Figure 11, a curve 291 shows the results of a deposition with the left hand target rotating clockwise and the right hand target rotating counterclockwise, opposite to the directions indicated on Figure 8. A curve 293, on the other hand, shows the results of a deposition with the targets rotated in the directions shown on Figure 8. It can be seen that the choice of the rotation direction discussed above with respect to Figure 8 considerably flattens out the element concentration curve. A perfectly flat concentration curve is the goal for obtaining a homogenous film deposition on a substrate that is moved along this deposition path beneath the targets. Such a flat curve is practically obtained by also varying the other parameters discussed above with respect to Figures 8-10, the results of Figure 11 showing the effect of rotation direction alone.

The experiments leading to the results shown in Figure 11 were conducted with one target surface of substantially pure zirconium having its magnet assembly positioned with its angle θ at 45 degrees, and the other target surface of substantially pure titanium having its magnet angle θ at 30 degrees. The targets were both rotated at 16 r.p.m. The DC power applied to the zirconium target was 1 kw, while the titanium target received 4 kw of power. The pressure in the vacuum chamber during deposition was about 4 mTorr.

Referring to Figure 12, a curve 295 shows the results by rotating tin and zinc targets at 1 r.p.m., and a curve 297 shows the results when the targets were

both rotated at 8 r.p.m. All other parameters were held fixed during the two experiments leading to the results of Figure 12. It can be seen that the higher speed desirably flattens out the concentration ratio curve 5 somewhat. Indeed, it appears that the targets of the experimental set-up should be rotated at 8 r.p.m. or more as an aid to reach the goal of depositing a homogeneous film.

10 The data shown in Figure 12 was obtained with the magnet angle θ of the tin target at 30 degrees, and that of the zinc target at 45 degrees. The DC power applied to the tin target was 600 watts, and that applied to the zinc target 500 watts. The pressure in the deposition chamber was about 15 mTorr.

15 Use of a Separate Contamination Target

20 The techniques of co-sputtering discussed above are highly useful and are significant improvements over methods not utilizing co-sputtering, but there is some disadvantage in that positioning the magnets with 25 a non-zero angle θ , or θ_2 , as illustrated in Figures 2 and 8, lowers the deposition rate and causes molecules formed from particles sputtered off of the targets to strike the substrate at an acute angle with the substrate. The densest films are obtained, generally, 25 when molecules strike the substrate perpendicularly with a high rate of deposition.

30 In further embodiments illustrated in Figures 13-14, the advantages of the co-sputtering techniques described above exist while still causing the film to be deposited at a high rate and at a normal angle with the substrate. This is illustrated generally in the configuration of Figure 13, a configuration that has been previously mentioned. This is perhaps better referred to as "cross-sputtering" since one sputtering source is provided solely for the purpose of depositing 35

its material only onto another sputtering source that is provided in turn to deposit material directly onto the substrate.

A first rotating cylindrical target assembly 5 301 of Figure 13 has a single material M3 in a target 303 and an internal magnet assembly 305 directed straight downward toward the path of a moving substrate 307. A second target assembly 309 having a target 311 with a different single material M4 includes an internal magnet assembly 313 that is rotated 90° from the vertical to face directly against the first target assembly 301. In this embodiment, the arrangement is made such that material is not sputtered directly from the target 311 onto the substrate 307. Rather, it is 10 first sputtered onto the target 303, and then the combination of the two target materials M3 and M4 is sputtered straight downward onto the substrate 307. 15

Thus, the configuration of Figure 13 maintains 20 the target assembly 301 to sputter material directly downward to deposit the densest possible film onto the substrate below. The advantages of co-sputtering are maintained, however, in that the two materials M3 and M4 of the targets 303 and 311 do not need to be alloyed into 25 a single target, as was heretofore the case, but rather can be maintained in separate targets. A baffle or the like (not shown) may be necessary in the embodiment of Figure 13 to prevent deposition of the material M4 onto the substrate directly from the target 311. The 30 relative proportions of the separate target materials M3 and M4 sputtered from the target 301 is controlled primarily by controlling the rate of deposition from the target 311 onto the target 303.

Since it has become desirable with the use of 35 rotating cylindrical magnetrons to use two of them side-by-side, such a configuration utilizing cross-sputtering is illustrated in Figure 14. Target assemblies 315 and

317 are positioned side-by-side and contain the same material M5 on the outside surface of their targets. The magnets internal of the cylindrical targets are directed straight downward to a substrate 319. A third 5 rotating cylindrical magnetron structure 321 is positioned above the other two and contains a different sputtering material M6 on the outside of its target from that on the target assemblies 315 and 317. A magnetic assembly 323 has its magnetic poles arranged so that 10 resulting erosion zones 325 and 327 are positioned opposite the targets of the assemblies 315 and 317. The material M6 is thus sputtered off the target of the assembly 321 and onto each of the targets of the assemblies 315 and 317, to be resputtered therefrom 15 along with material M5 on the lower-most targets. Alternatively, two targets can be employed in place of the target 321, one sputtering material onto the bottom target 315 and the other onto the bottom target 317. In order to prevent material from being sputtered directly 20 from the target assembly 321 and onto the substrate 319, some form of baffling, such as the baffle 329, may be desirable.

The configuration of Figure 14 operates by maintaining two plasmas. The targets of the assemblies 25 315 and 317 form a first cathode and gases are introduced by conduits 316 and 317 to support its plasma. The target of the assembly 321 forms a second cathode and gases introduced through conduits 322 and 324 support its plasma. It will be recognized that many 30 alternative numbers and arrangements of targets are possible to implement the cross-sputtering improvements of the present invention.

Referring to Figure 15, a modification of the system of Figure 14 is shown. In place of the rotating 35 cylindrical magnetron 321 of Figure 14, a planar magnetron assembly 331 is utilized. It has a planar

target surface 333 of material M6 and a magnetic assembly (not shown) configured to create a race track having erosion zones 337 and 339 facing respective rotating target assemblies 315 and 317 to cause particles sputtered therefrom to form a film on the cylindrical targets. The erosion zones 337 and 339 are preferably aligned with the axis of rotation of the respective target assemblies 315 and 315 in the view shown, and extend substantially the entire length of the 10 cylindrical targets in a direction perpendicular to the paper. A plasma is supported around the planar target surface 333, forming a second cathode, by gasses introduced through conduits 341 and 343.

Although the invention has been described with 15 respect to its preferred embodiments, it will be understood that the invention is to be protected within the full scope of the appended claims.

IT IS CLAIMED:

1. A method for depositing a substantially homogeneous film on a substrate within an evacuated chamber, comprising the steps of:
 - (a) providing a first target member carrying on an outer surface thereof a first sputtering material;
 - (b) providing a second target member carrying on an outer surface thereof a second sputtering material different from the first sputtering material;
 - (c) introducing a gas into the chamber,
 - (d) applying an electrical potential to the first and second target members, thereby to cause sputtering of the first and second materials therefrom; and
 - (e) positioning the first and second target members relative to each other and to said substrate to cause the first material sputtered from the first target to be deposited on the outer surface of the second target and the second material sputtered from the second target to be deposited on the outer surface of the first target in a manner that material sputtered from each of the first and second targets onto the substrate is substantially the same combination of the first and second materials, whereby a substantially homogeneous film of said first and second materials is deposited on the substrate.
2. The method of claim 1 wherein each of said first and second target members comprise elongated tubular members mounted horizontally in said evacuated chamber, wherein in each tubular member a magnetic field is provided to form a sputtering zone on said sputtering material extending substantially the entire length of the tubular member and circumferentially along a relatively narrow region thereof, wherein each tubular

10 member is rotated about its longitudinal axis, and wherein said tubular members are situated substantially parallel to each other.

3. The method of claim 2 wherein the step of positioning the first and second target members includes the steps of aligning the magnetic field in the first tubular member so that some of the first sputtering material sputtered from the first target member is deposited onto the second target and aligning the magnetic field in the second tubular member so that some of the second sputtering material sputtered from the second target member is deposited onto the first target.

4. The method of claim 3 wherein the first and second sputtering material is selected from a group consisting of aluminum, indium, nickel, silicon, tantalum, tin, titanium, zinc, and zirconium.

5. The method of claim 1 which additionally comprises the step of: (e) moving said substrate relative to said target members.

6. In a method of coating a substrate moving through a deposition zone in a reactive sputtering chamber wherein two adjacent cylindrically shaped targets are rotated about their respective axes that are substantially parallel to each other and wherein each target contains a stationary magnetic assembly that confines a sputtering zone to an elongated and narrow sputtering region through which the target surfaces rotate, an improvement comprising:

10 causing each of the two target surfaces to have different materials; and

orienting the sputtering zone of at least one of the two targets to cause some material sputtered from

15 one target surface to be deposited onto the other target surface in a manner that the composition of the material deposited onto the substrate from the erosion zones of the targets consists substantially of the same combination of the different materials of the two target surfaces, whereby the film formed on the substrate is a homogeneous 20 combination of the different sputtered materials.

7. The method according to claim 6 wherein the improvement additionally comprises the step of rotating said targets in opposite directions with adjacent outside surfaces thereof moving in a common 5 direction away from said substrate.

8. In a method of coating a substrate moving through a deposition zone in a reactive sputtering chamber wherein two adjacent cylindrically shaped targets are rotated about their respective axes that are 5 substantially parallel to each other, each of the targets contains an adjustable magnetic assembly that confines a sputtering zone to a selected elongated and narrow sputtering region through which the target surfaces rotate, and electrical power is applied to each 10 target, an improvement comprising the steps of:

causing each of the two target surfaces to have different materials;

15 rotating said targets in opposite directions with adjacent outside surfaces thereof moving in a common direction away from said substrate;

adjusting various parameters of operation of said first and second targets in a manner to cause the film formed on the substrate to be a homogeneous combination of the different sputtered materials, said 20 adjusting step including the steps of:

adjusting a rotatable position of the magnets within said first and second tubular

members, thereby to position their respective sputtering zones;

25 adjusting a speed of rotation of said first and second tubular members; and

adjusting the power to each of the first and second tubular members.

9. The method according to claim 8 wherein the adjusting step include the steps of individually adjusting the speed of rotation of said first and second tubular members.

10. The method according to claim 8 wherein the adjusting step includes making said adjustments so that material is sputtered from one target surface and deposited onto the other target surface in a manner that

5 the composition of the material deposited onto the substrate from the erosion zones of the each of said first and second targets consists substantially of the same combination of the different materials of the two target surfaces.

11. The method according to claim 8 wherein the first and second sputtering material is selected from a group consisting of aluminum, indium, nickel, silicon, tantalum, tin, titanium, zinc, boron, tungsten, niobium, hafnium, magnesium, silver, ruthenium, vanadium, chromium, molybdenum, bismuth, and zirconium.

12. The method according to claim 8 wherein the magnetic rotation step includes the steps of positioning the magnets within each of the first and second tubular members in a direction toward the other 5 tubular member at an angle within a range of approximately 25° to 90° from normal.

13. An apparatus for depositing a substantially homogeneous film on a large dynamic substrate, comprising:

(a) an evacuable coating chamber;
5 (b) a first cathode assembly mounted in said coating chamber, said first cathode assembly including a first elongated, cylindrical tubular member rotatable about an axis thereof and having a layer of a first material to be sputtered carried by an outer surface thereof;

10 (c) a second cathode assembly mounted in said coating chamber and substantially parallel to said first cathode assembly, said second cathode assembly including a second elongated, cylindrical tubular member rotatable about an axis thereof and having a layer of a second material to be sputtered carried by the outer surface thereof, said second material being different from said first material;

15 (d) magnetic means located in each of said first and second tubular members for providing a sputter zone extending substantially the entire length of each of said first and second tubular members and circumferentially along a relatively narrow region thereof;

20 (e) means for rotating each of said first and second tubular members about their respective longitudinal axes to bring different portions of the outer surfaces thereof into sputtering position opposite said magnetic means and within said sputtering zone;

25 (f) means for moving said substrate along a path within said coating chamber past said first and second cathode assemblies; and

30 (g) wherein the magnetic means in the first cathode assembly is disposed at an angle so that some of the first coating material that is sputtered from the first cathode is deposited onto the second cathode and

40 the magnetic means in the second cathode assembly is disposed at an angle so that some of the second coating material that is sputtered from the second cathode is deposited onto the first cathode in a manner that material sputtered from each of the first and second cathodes and onto said substrate path is substantially the same combination of the first and second materials.

14. The apparatus of claim 13 wherein the magnetic means in the first cathode assembly is disposed toward the second cathode assembly at an angle of approximately 25° to 90° from normal and wherein the 5 magnetic means in the second cathode assembly is disposed toward the first cathode assembly at an angle of approximately 25° to 90° from normal.

15. The apparatus of claim 13 wherein the first and second materials are selected from a group consisting of aluminum, indium, nickel, silicon, tantalum, tin, titanium, zinc, boron, tungsten, niobium, 5 hafnium, magnesium, silver, ruthenium, vanadium, chromium, molybdenum, bismuth, and zirconium.

16. The apparatus of claim 13 which additionally comprises:

means operably connected to said rotating means for controlling the speed of rotation of said 5 first and second tubular members,

means coupled with the magnetic means for individually adjusting an angular position of said magnetic means within their respective first and second tubular members, thereby to position said sputtering 10 zones,

means coupled with each of said first and second cathode assemblies for individually controlling the amount of DC power applied to each, and

15 wherein said rotating means is characterized by rotating said first and second tubular members in opposite directions with their opposing outside surfaces moving in a common direction away from said substrate path.

17. The apparatus of claim 16 wherein said speed controlling means includes means for individually controlling the speed of rotation of each of the first and second tubular members.

18. Apparatus for depositing a substantially homogeneous film on a large dynamic substrate, comprising:

- (a) an evacuable coating chamber;
- 5 (b) a first elongated, cylindrical tubular member rotatable about an axis thereof within said chamber and having a layer of a first material to be sputtered carried by an outer surface thereof;
- (c) a second elongated, cylindrical tubular member rotatable about an axis thereof within said chamber and having a layer of a second material to be sputtered carried by the outer surface thereof, said second material being different from said first material, the first and second tubular members being positioned adjacent to each other;
- 10 (d) first and second magnetic means located respectively in each of said first and second tubular members for providing a sputter zone extending substantially the entire length of each of said first and second tubular members and circumferentially along a relatively narrow region thereof;
- 15 (e) means for rotating each of said first and second tubular members about their respective longitudinal axes to bring different portions of the outer surfaces thereof into sputtering position opposite said magnetic means and within said sputtering zone;

30 (f) means for individually adjusting the first and second magnetic means to control the circumferential position of their sputter zones about their respective first and second tubular members;

(g) means for providing power to each of the first and second tubular members;

35 (h) means for moving said substrate along a path within said chamber past said first and second tubular members; and

40 (i) means coupled with said tubular member rotating means, said magnetic adjusting means and said power means for adjusting the speed of rotation of the first and second tubular members, adjusting the position of the first and second magnetic means and individually adjusting the power applied to said first and second tubular members for causing to be directed toward said substrate path substantially the same proportions of said first and second materials from each of said first and second tubular members, whereby a homogeneous film 45 is deposited onto said substrate.

19. An apparatus for depositing a substantially homogeneous film on a large dynamic substrate, comprising:

5 (a) an evacuable coating chamber;

(b) a first cathode mounted in said coating chamber comprising an elongated, cylindrical tubular member having a layer of first coating material to be sputtered applied to the outer surface thereof;

10 (c) a second cathode mounted in said coating chamber and substantially parallel to said first cathode comprising an elongated, cylindrical tubular member having a layer of second coating material to be sputtered applied to the outer surface thereof;

15 (d) magnetic means located in each of said first and second cathodes for providing a sputtering

zone extending substantially the entire length of the tubular member and circumferentially along a relatively narrow region thereof, said magnetic means being rotatably positionable to cause their respective sputtering zones being located in excess of 25 degrees from a downward position in a direction toward the other cathode;

20 (e) means for rotating each of said cathodes about its longitudinal axis to bring different portions of the outer surface thereof into sputtering position opposite said magnetic means and within said sputtering zone, said rotating means causing said cathodes to rotate in opposite directions away from each other at their downward position; and

25 (f) means for moving said substrate along a path within said coating chamber underneath said first and second cathodes.

20. A method of depositing on a substrate a film having a composition including first and second materials, comprising the steps of:

5 providing at least one rotatable cylindrical target having said first material carried on an outer surface thereof but not said second material,

10 positioning a magnetic assembly within said at least one target to cause a sputtering zone to be positioned substantially directly opposite said substrate,

15 rotating the outer target surface of said at least one target through said sputtering zone with an electrical potential applied thereto, and

depositing the second material on the outer surface of said at least one target in a position removed from said sputtering zone and without depositing any substantial amounts of the second material directly on said substrate, whereby a combination of the first and second materials is sputtered from said at least one target and onto the substrate.

21. A method of depositing on a substrate by sputtering a film having a composition including first and second materials, comprising the steps of:

- 5 providing a first rotatable cylindrical target having said first material carried on an outer surface thereof but not said second material,
- 10 positioning adjacent the first target a second rotatable cylindrical target also having said first material carried on an outer surface thereof but not said second material,
- 15 positioning a magnetic assembly within each of said first and second targets in a manner to cause a sputtering zone to be positioned on the outside of each of said first and second targets substantially directly opposite said substrate,
- 20 rotating the outer surfaces of said first and second targets through said sputtering zone with an electrical potential applied thereto, and
- 25 depositing the second material on the outer surface of each of said first and second targets in positions removed from their respective sputtering zones and without depositing any substantial amounts of the second material directly on said substrate,

whereby a combination of the first and second materials is sputtered onto the substrate from the sputtering zones of said first and second targets.

22. The method according to claim 21 wherein the step of depositing the second material includes positioning adjacent the first and second targets a third rotatable cylindrical target having said second material carried on an outer surface thereof, and positioning within the third target a magnetic assembly that defines sputtering zones on the outside of the third target opposite said first and second targets.

23. The method according to claim 21 wherein the step of depositing the second material includes positioning adjacent the first and second targets a planar magnetron having sputtering zones opposite said first and second targets.

5 24. An apparatus for depositing a substantially homogeneous film on a substrate, comprising:

an evacuable coating chamber having means for supporting the substrate;

10 a pair of rotatable cylindrical magnetron sputtering targets positioned in said coating chamber adjacent each other and said substrate supporting means, each of said targets having a layer of a first material to be sputtered applied to the outer surfaces thereof but substantially omitting a second material to be sputtered;

15 a magnetic structure located in each of said first and second targets to provide a sputtering zone extending substantially an entire length of each target and circumferentially along a relatively narrow region thereof, said magnetic structures being rotatably positioned to cause their respective sputtering zones to both face substantially directly toward said substrate supporting means,

20 means rotating each of said targets for passing different portions of the outer surfaces thereof through their respective sputtering zones, and

25 means positioned adjacent said first and second targets for depositing thereon a film of said second material, whereby a combination of said first and second materials can be deposited onto the substrate from said sputtering zones of said first and second targets.

25. The apparatus of claim 24 wherein said second material depositing means includes a third rotating cylindrical target having on an outside thereof said second material but substantially omitting said 5 first material.

26. The apparatus of claim 24 wherein said second material depositing means includes a planar magnetron having a target of said second material but substantially omitting said first material.

1/8

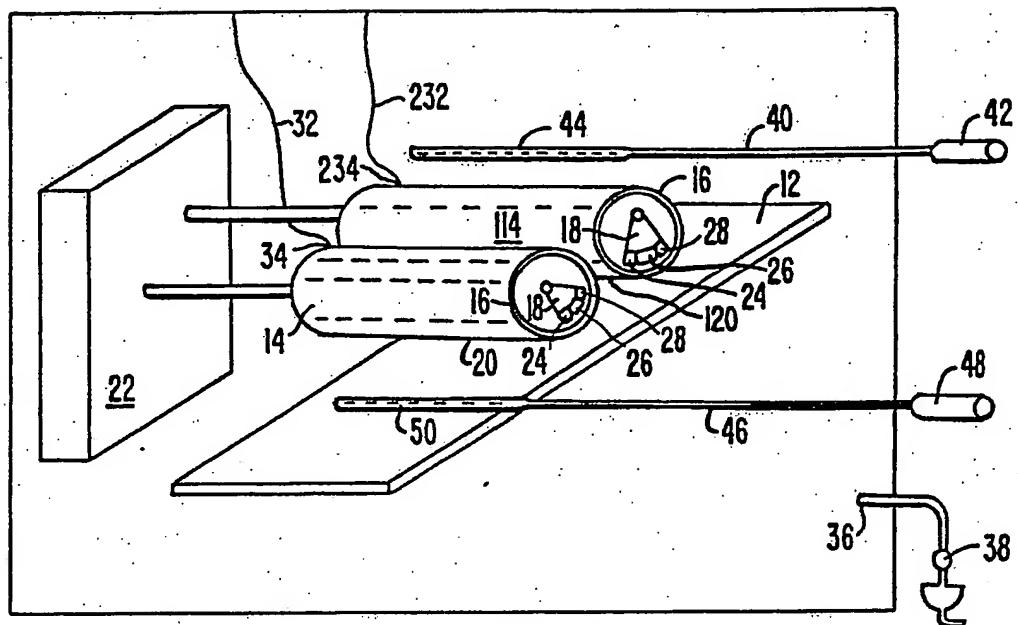


FIG. 1.

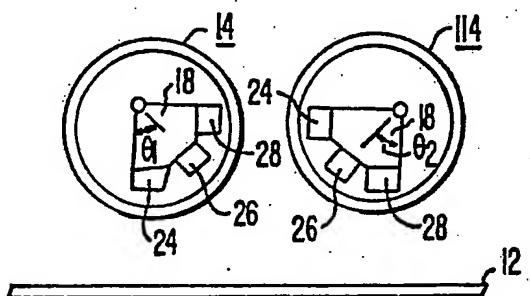


FIG. 2.

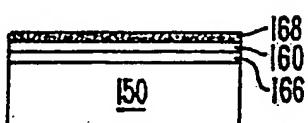
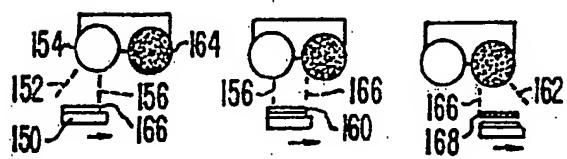


FIG. 3.

2/8

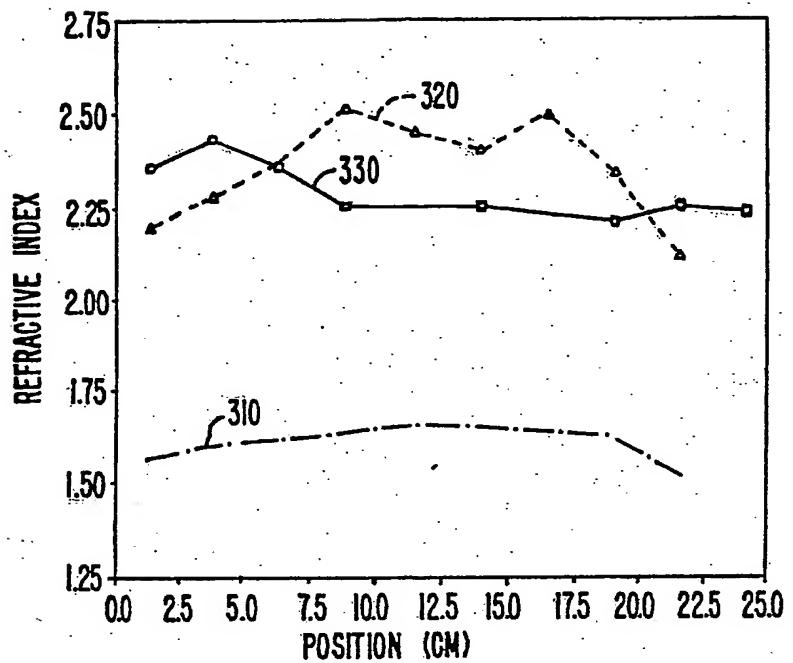


FIG. 4.

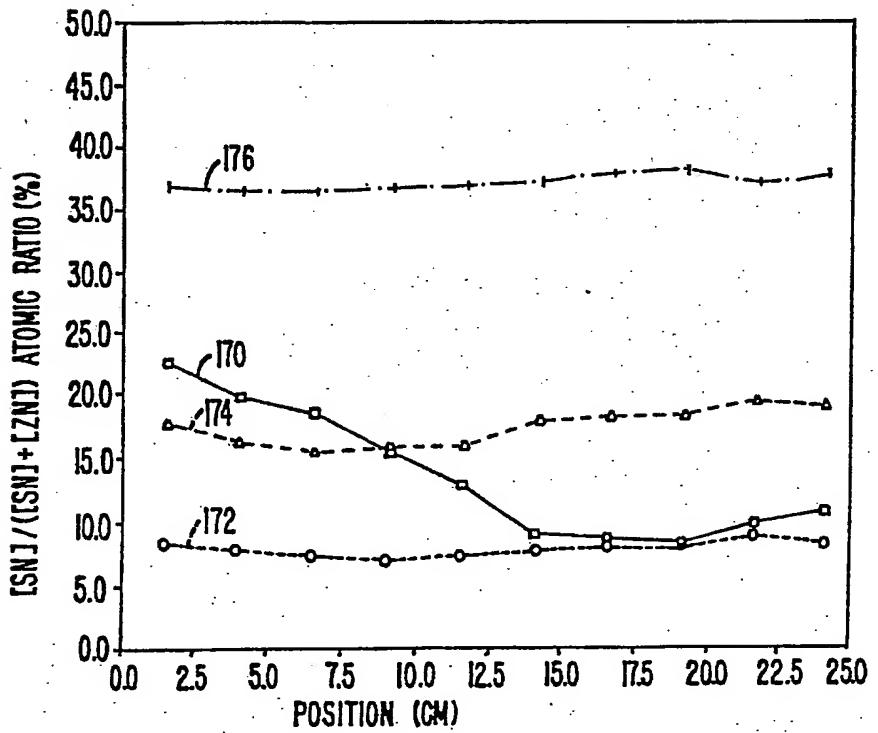


FIG. 5.

3/8

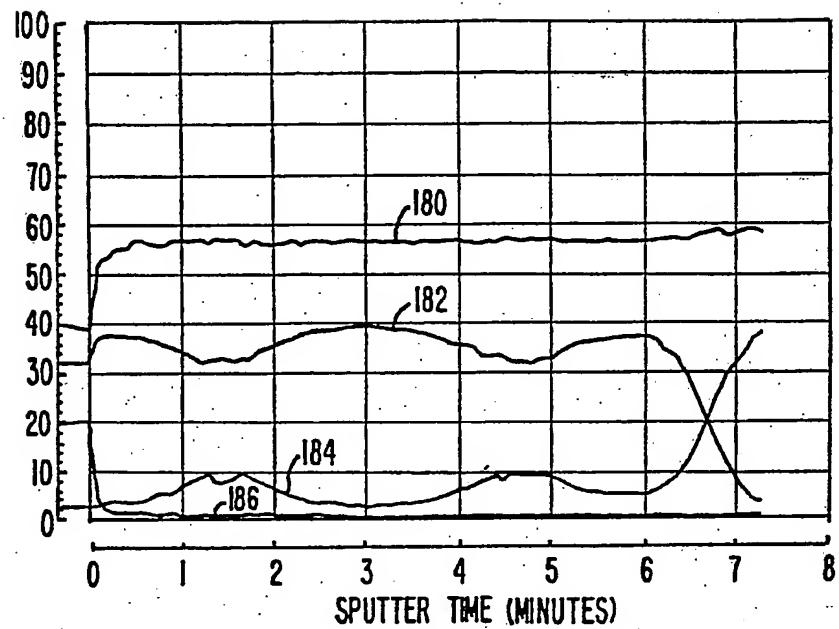


FIG. 6.

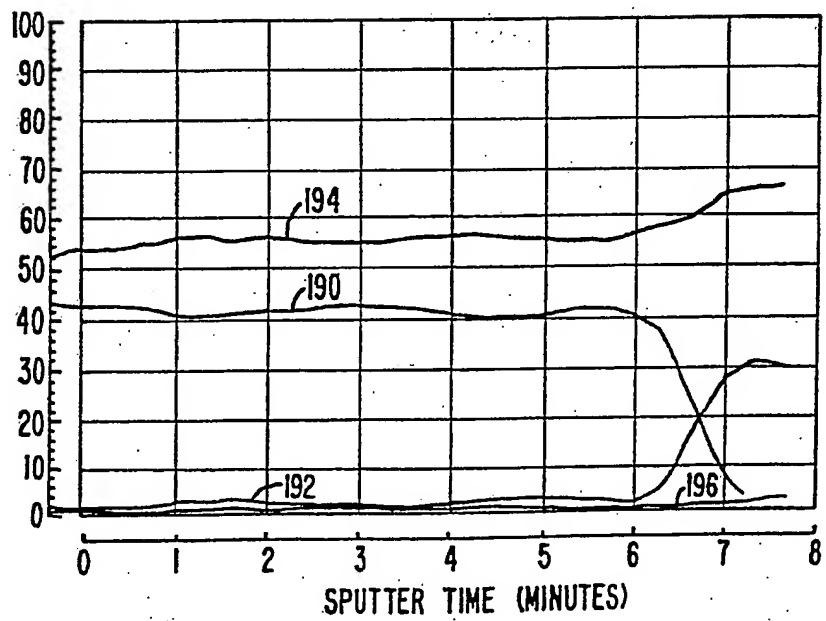


FIG. 7.

4/8

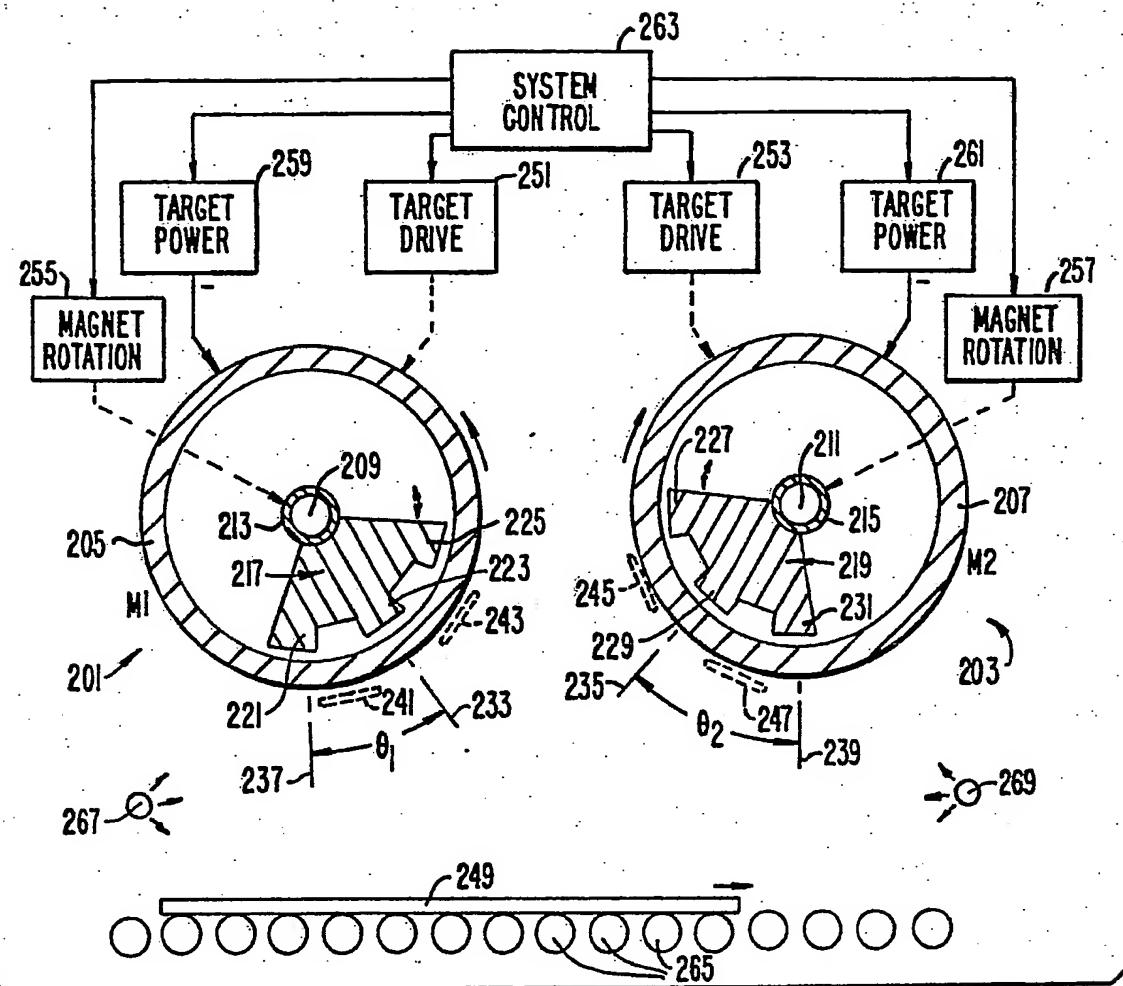
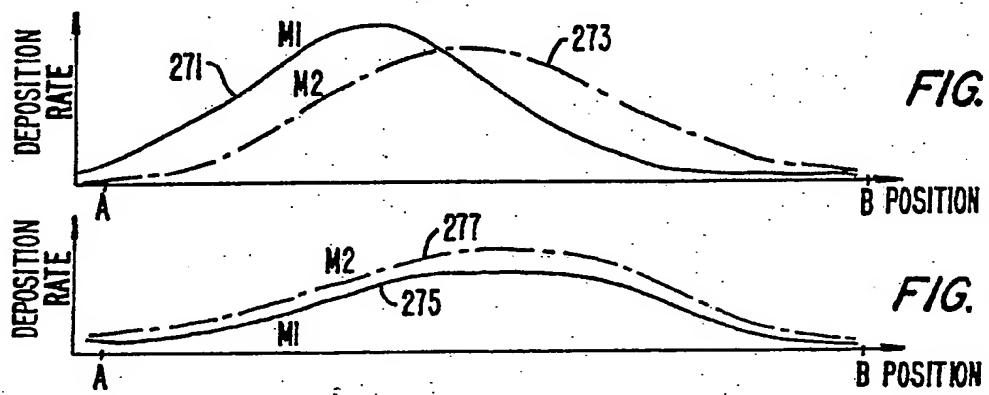


FIG. 8.



5/8

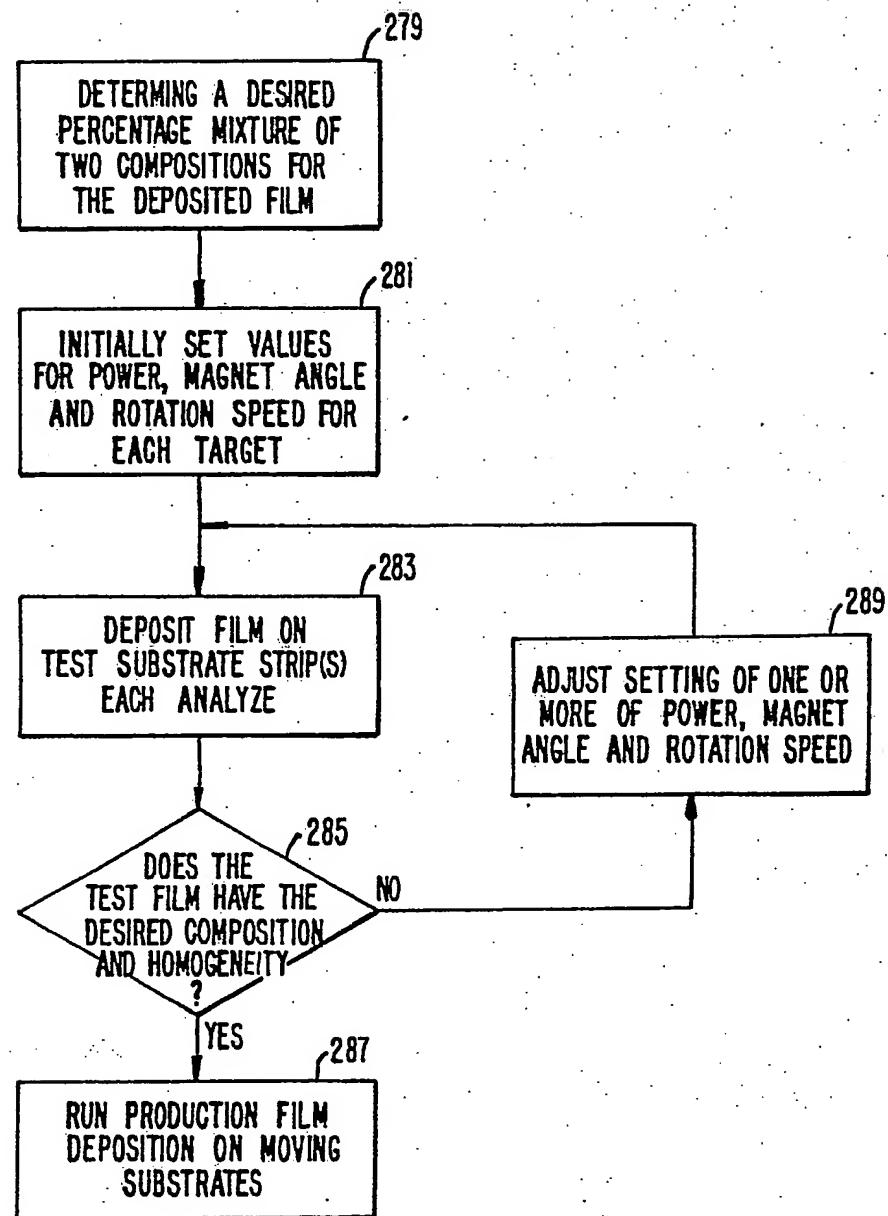


FIG. 10.

6/8

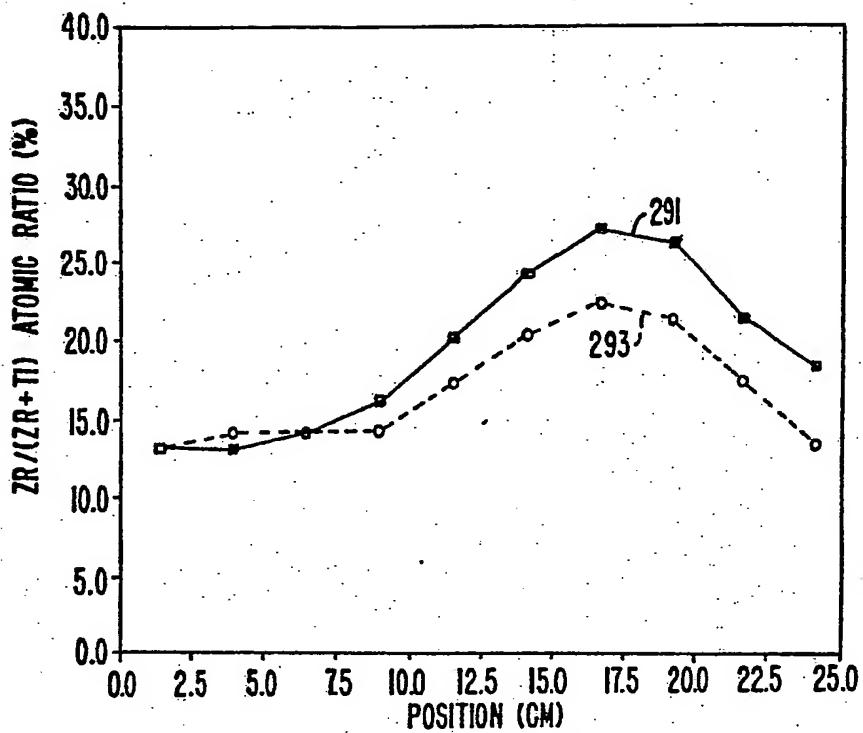


FIG. 11.

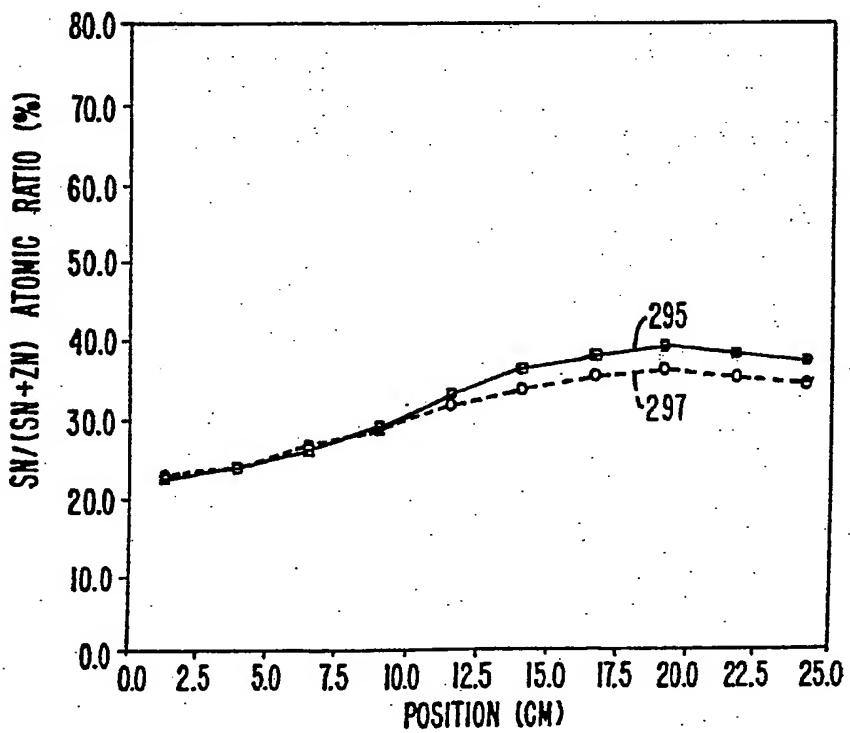


FIG. 12.

7/8

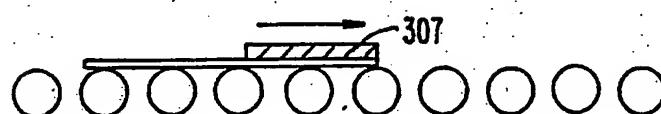
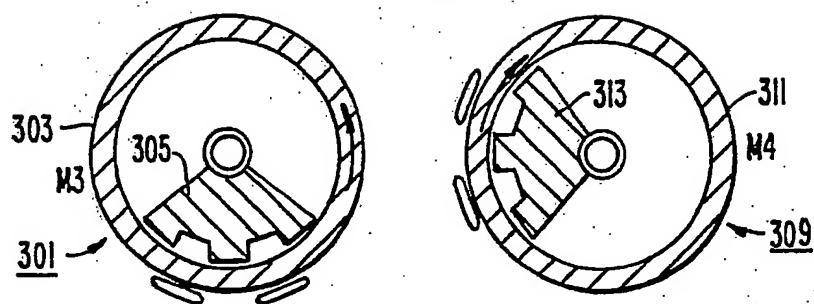


FIG. 13.

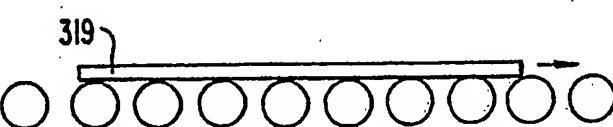
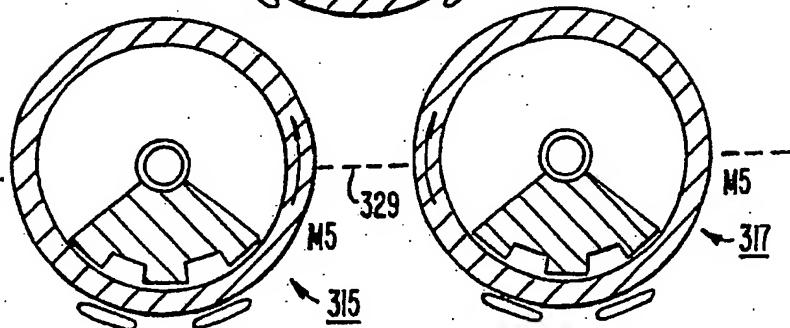
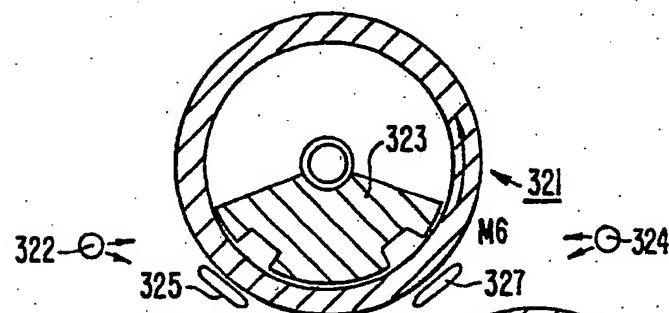


FIG. 14.

8/8

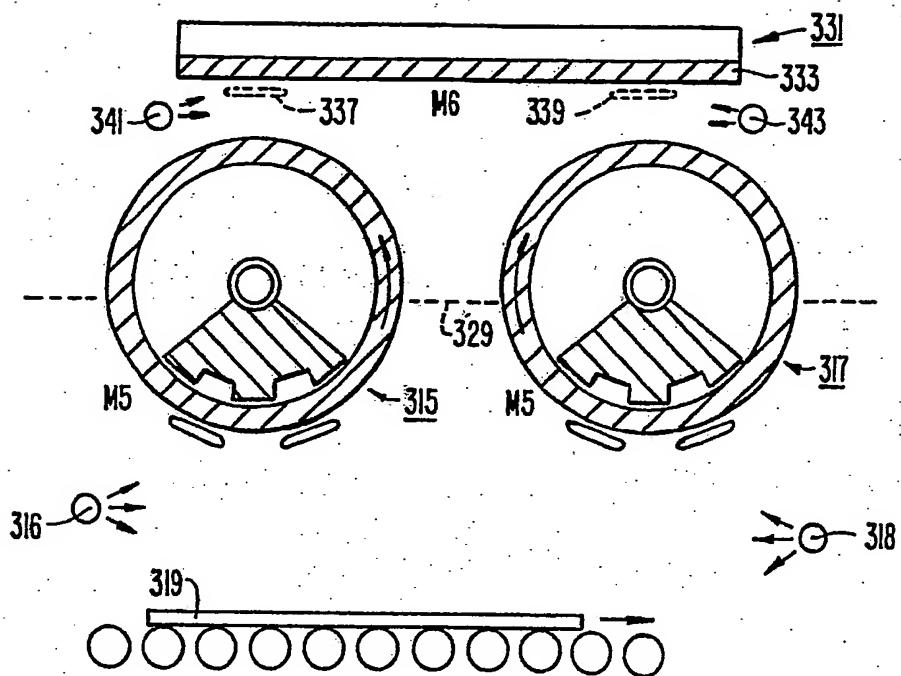


FIG. 15.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US91/04738

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁸

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC(5): C23C 14/34
 US CL : 204/298.21

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
U.S.	204/192.12,298.03,298.16,298.21,298.22,298.23,298.28

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X Y	J. Hanak, "Co-sputtering-Its limitations and possibilities", Le vide, No. 175,1975, p.11-18, see pages 11-13.	1 2-7,13-15 and 19-26
X Y	US,A 4,885,070 (CAMBELL et al) 05 December 1989, See the entire document	1 2-7,13-15 and 19-26
Y	US,A 4,466,877 (MCKELVEY) 21 August 1984, See the entire document	1,2-7,13-15 and 19-26
Y	US,A 4,166,783 (TURNER) 04 September 1979, See figure 2 and columns 2-3	8-12 and 16-18
Y	US,A 4,595,482 (MINTZ) 17 June 1986, See figure 1	8-12 and 16-18

- Special categories of cited documents: ¹⁰
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

10 September 1991

Date of Mailing of this International Search Report

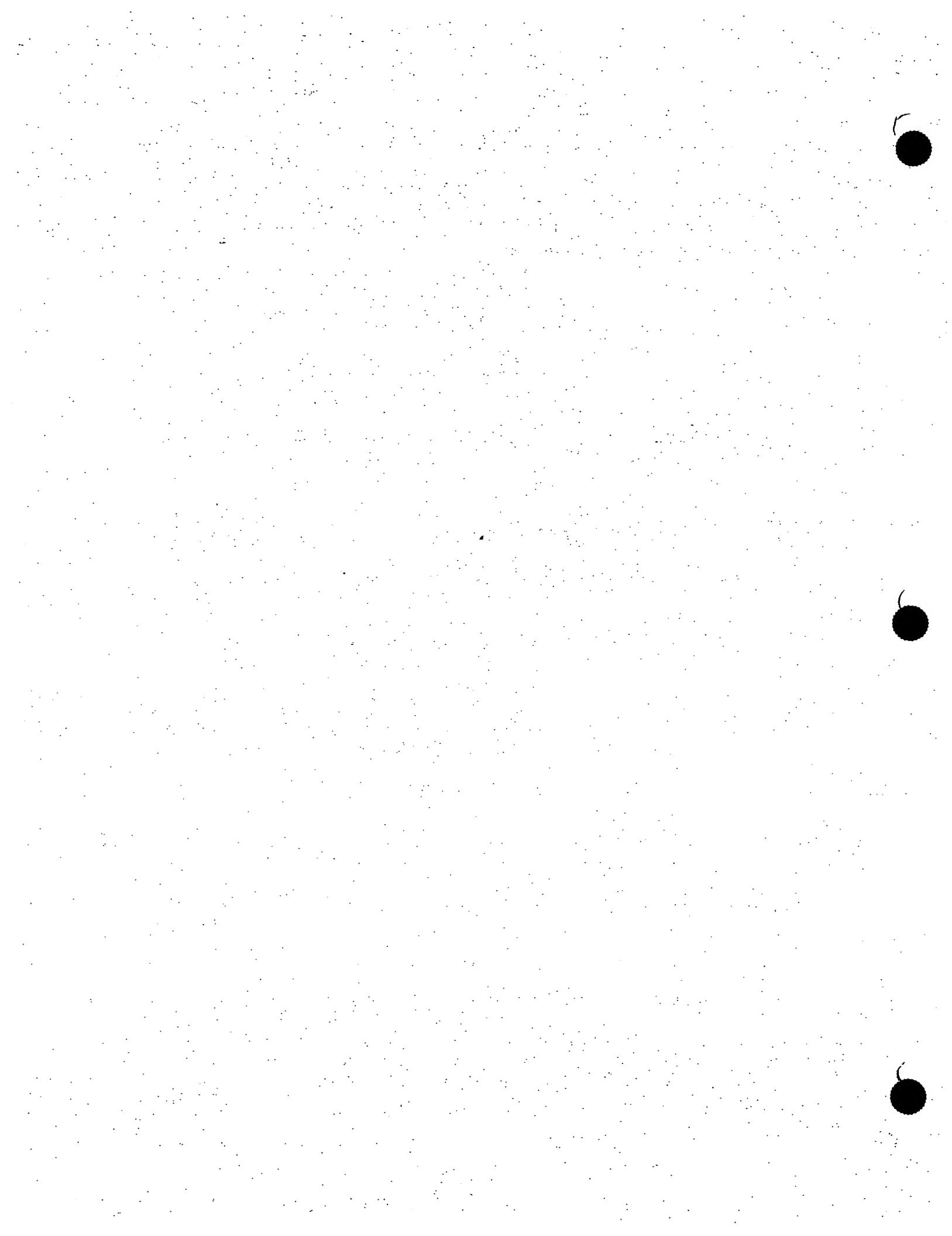
04 OCT 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

N. Nguyen



[Zurück zur Hauptseite](#)

Kategorie:	A2	Anmelder	BOC		
Titel:	Device and Method for Co-Sputtering and cross-sputtering homogeneous Films				
Prio-Datum:	06.07.90	Prio-Land:	US	Prio-Nr.:	549.392
US-Nr.:				Status:	
EP-Nr.:	WO 92/01081			Status:	keine nationalen Anmeldungen
DE-Nr.:				Status :	
Kommentar	Vorrichtung enthält zwei Targets aus unterschiedlichen Materialien, um ein Substrat mit einer Mischung aus beiden Materialien zu beschichten. Zuvor beschichten sich aber beide Targets gegenseitig.				
EP-Anspruch:	Keine Schutzrechte in den einzelnen Ländern. PCT-Verfahren wurde nicht weitergeführt.				

Rechtsstand

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)